Sulphur isotope constraints on formation conditions of the Luiswishi ore deposit, Democratic Republic of Congo (DRC)

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Dedicated to Prof. A.B. Kampunzu

Abstract

Luiswishi is a Congo-type Neoproterozoic sediment-hosted stratiform Cu–Co ore deposit of the Central Africa Copperbelt, located northwest of Lubumbashi (DRC). The ores form two main Cu–Co orebodies hosted by the Mines Subgroup, one in the lower part of the Kamoto Formation and the other at the base of the Dolomitic Shales Formation. Sulphides occur essentially as early parallel layers of chalcopyrite and carrolite, and secondarily as late stockwork sulphides cross-cutting the bedding and the early sulphide generation. Both types of stratiform and stockwork chalcopyrite and carrolite were systematically analyzed for sulphur isotopes, along the lithostratigraphic succession of the Mine Series. The quite similar $\delta^{34}S$ values of stratiform sulphides and late stockwork sulphides suggest an in situ recrystallization or a slight remobilization of stockwork sulphides without attainment of isotopic equilibrium between different sulphide phases (chalcopyrite and carrolite). The distribution of $\delta^{34}S$ values (−14.4‰ to +17.5‰) combined with the lithology indicates a strong stratigraphic control of the sulphur isotope signature, supporting bacterial sulphate reduction during early diagenesis of the host sediments, in a shallow marine to lacustrine environment. Petrological features combined with sulphur isotopic data of sulphides at Luiswishi and previous results on nodules of anhydrite in the Mine Series indicate a dominant seawater/lacustrine origin for sulphates, precluding a possible hydrothermal participation. The high positive $\delta^{34}S$ values of sulphides in the lower orebody at Luiswishi, hosted in massive chloritic–dolomitic siltite (known as Grey R.A.T.), fine-grained stratified dolostone (D.Strat.) and silicified-stromatolitic dolomites alternating with chloritic-dolomitic silty beds (R.S.F.), suggest that they were probably deposited during a period of regression in a basin cut off from seawater. The variations of $\delta^{34}S$ values (i.e. the decrease of $\delta^{34}S$ values from the Kamoto Formation to the overlying Dolomitic Shales and then the slight increase from S.D.2d to S.D.3a and S.D.3b members) are in perfect agreement with the inferred lithological and transgressive–regressive evolution of the ore-hosting sedimentary rocks [Cailteux, J., 1994. Lithostratigraphy of the Neoproterozoic Shaba-type (Zaire) Roan Supergroup and metallogenesis of associated stratiform mineralization. In: Kampunzu A.B., Lubala, R.T. (Eds.), Neoproterozoic Belts of Zambia, Zaire and Namibia. Journal of African Earth Sciences 19, 279–301].

Keywords: Central Africa Copperbelt; Luiswishi; DRC; Mineralogy; Sulphur isotopes

1. Introduction

The giant Cu–Co metallogenic province of Central Africa extends for ±700 km in the Democratic Republic of Congo (DRC) and Zambia (Fig. 1). It lies within the Pan-African Lufilian fold arc, formed by tectonic compression of the Neoproterozoic Katangan sedimentary basin, related to the convergence between the Congo and the Kalahari Cratons (Demesmaeker et al., 1963; Cahen, 1974; Kampunzu and Cailteux, 1999). The stratiform copper ore deposits are confined to the Roan Group both in Congo and Zambia. In Congo, most of the Cu–Co

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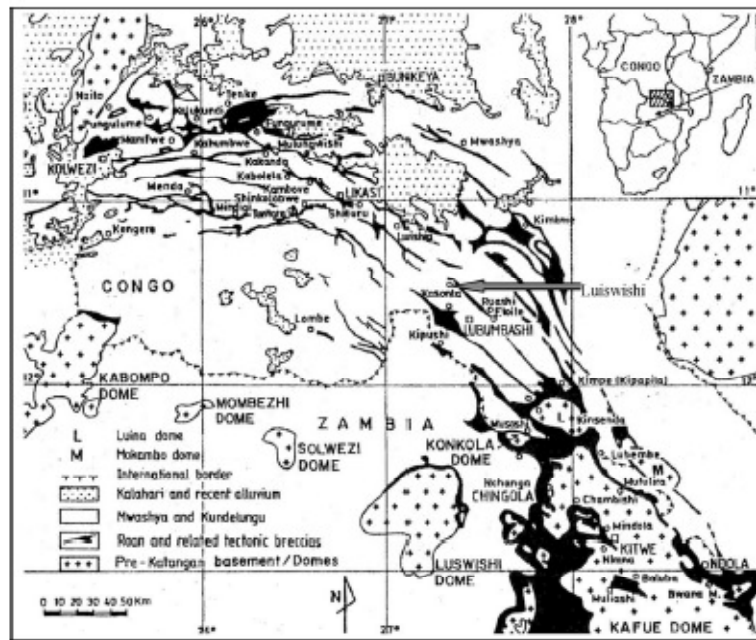Φ Deceased on 29 November 2004.

Fig. 1. Lufilian arc in Democratic Republic of Congo and Zambia (modified from Cailteux et al., 1994). Location of the main deposits (circles) and of the Luiswishi deposit.

deposits are hosted by the Mines Subgroup (Oosterbosch, 1962; François, 1974). The ore includes chalcopyrite, bornite, chalcocite, carrolite with (Co, Ni) pyrite (Bartholomé, 1962; Oosterbosch, 1962; Bartholomé et al., 1971; Cailteux, 1986, 1994). The genesis of the copper–cobalt ores still remains under debate, with theories ranging from hydrothermal-diagenetic to syngenetic-diagenetic (Mendelsohn, 1961; Garlick, 1967, 1989; Bartholomé et al., 1972; Bartholomé, 1974; Ohmoto, 1986; Unrug, 1988; Annels, 1989; Sweeney et al., 1991; Cailteux et al., this issue).

Several stable isotope datasets from the Copperbelt deposits have been reported in the literature (Dechow and Jensen, 1965; Okitaudji-Lokoho, 1989; Ohmoto, 1986; Sweeney et al., 1986, 1991) but only a few papers give isotopic profiles along the lithological succession and with a good correlation with the stratigraphic column. In particular, sulphur isotopes of the sulphides documented regressive-transgressive sequences in the Zambia-type orebodies (Sweeney et al., 1986, 1991), that were shown to be lateral correlatives of the Congo-type Cu–Co orebodies (Cailteux et al., 1994).

The objective of this paper, based on petrological observations and sulphur isotope analyses of sulphides from borehole samples of the Luiswishi Cu–Co deposit (DRC), is to constrain the ore genesis related to sedimentological and/or structural processes, and to compare the presented data with previous works on other stratiform copper ore deposits of the Copperbelt and of the world.

2. Geological setting of the Luiswishi ore deposit

Discovered in 1913 and located 26 km northwest of Lubumbashi (DRC), Luiswishi is one of the Congo-type Neoproterozoic sediment-hosted stratiform Cu–Co ore deposits of the Central Africa Copperbelt (Cailteux, 1994; Cailteux et al., 2003, this issue). The ores are hosted in Neoproterozoic Katangan sedimentary sequences that were affected by north verging folding and thrusting during the Pan-African Lufilian orogeny (Kampunzu and Cailteux, 1999). The Luiswishi deposit is part of a NW–SE-elongated and NE-directed thrust sheet lying in sedimentary rocks of the Kundelungu Group (Cailteux et al., 2003).

The Mines Subgroup lithostratigraphic succession intersected in the Luiswishi deposit is shown in Table 1 (Cailteux et al., 2003). It is a dolomitic sequence marked by transgressive (Kamoto and Dolomitic Shales Formations) and regressive (Kambove Formation) episodes. Quartz + carbonate pseudomorphs after anhydrite/gypsum and abundant magnesite indicate evapouritic conditions. The sedimentological features point to an intertidal sabkha-type depositional environment (Cailteux, 1978, 1994; Lefebvre, 1979).

Table 1
Lithology of the Katangan Supergroup and Mines Subgroup at Luiswishi, and position of the orebodies (according to Cailteux et al., 2003)

GROUP	SUB-GROUP	FORMATION	MEMBER	Lithologies	Cu-Co	
Kundelungu (formerly Upper Kundelungu)	Plateaux	Kambove Dolomite (formerly C.M.N.)	Upper	Pink-brown to white dolomite, talceous dolomite, evaporitic breccia, red siltstone		
	Kiubo			Dolomite, stromatolites, talceous dolomite, evaporitic breccia, grey-green siltstone		
	Kalule			Pink-brown to white massive dolomite	3rd OB (lenses)	
Nguba (formerly Lower Kundelungu)	Monwezi		Lower	Massive stromatolitic dolomites, crypto-algal & laminated talceous dolomite		
	Likasi			Laminated algal dolomite		
	Mwashya			Massive dolomite, stromatolites, dolomitic shale		
Roan	Dipeta	Dolomitic Shales	S.D.3b	Carbonaceous dolomitic shale		
	Mines		S.D.3a	Dolomitic shale, shaly dolomites		
	R.A.T.		S.D.2d	Carbonaceous dolomitic shale		
Base of the R.A.T. sequence unknown			S.D.2b-2c	Dolomitic shale, shaly dolomite		
± 900 Ma Basal conglomerate			S.D.2a	Carbonaceous dolomitic shale		
			B.O.M.Z.	Black ore mineralized zone	Upper OB	
			S.D.B.	Basal dolomitic shale		
		Kamoto Dolomite	R.S.C.	Roche siliceuse cellulaire		
			R.S.F.	Roche siliceuse feuilletée	Lower OB	
			D. Strat.	Stratified dolomite		
			Grey R.A.T.	Grey-green siltstone		

As for most of the Cu–Co deposits in Congo (Cailteux et al., this issue, and references therein), the Luiswishi ores form two main Cu–Co orebodies hosted by the Mines Subgroup, one in the lower part of the Kamoto Formation and the other at the base of the Dolomitic Shales Formation (code S.D.). The two orebodies are separated by a commonly sub-economic silicified stromatolitic dolomite (R.S.C., "Roche Siliceuses Cellulaires" Member) known for more than 300 km, along strike. Minor discontinuous low grade sulphide ore occurrences are known in similar lithologies of the Kambove Formation ("third orebody"; Table 1), giving rise to oxide ores in the weathered zone, representing ~9% of the total proved reserves in the deposit. The presence of organic matter (e.g., carbonaceous beds locally in Kamoto Formation; S.D.2a, 2d, 3b beds in Dolomitic Shales Formation) and stromatolites (e.g., in R.S.C. Member) indicate a reducing environment. The primary mineralisation intersected in the deepest part of the deposit includes mainly stratiform disseminated chalcopyrite and carrolite with minor pyrite and bornite (Cailteux et al., 2003). These sulphides occur in variable amounts in the Kamoto Formation and in the lower part of the Dolomitic Shales Formation. (Co–Ni) pyrite, siegenite, carrolite or polydymite also occur in the lower and upper orebodies from the eastern part of the deposit (Loris, 1996). Secondary sulphide mineralisation occurs in the orebodies as veinlets and stockworks cross-cutting the primary stratiform mineralisation. Mineralogically, this second generation of sulphide ores is quite similar to primary ore, and its origin is attributed to sulphur remobilizations during the Pan-African Lufilian tectonometamorphic events (Kampunzu and Cailteux, 1999; Cailteux et al., this issue).

3. Sampling and petrography

Very fresh samples were collected, mainly from drill-hole LSW1227 which exhibits a representative set of the different lithostratigraphic units, and from related sulphides at the scale of the deposit (Fig. 2). Two other samples were collected from drill-hole LSW1215, and two others from the surface, to complete the sampling. In the uppermost Kambove Formation, sulphides are very fine-grained disseminated pyrite with minor sphalerite, hosted in dolomite. In the upper part of the Dolomitic Shales Formation, some chalcopyrites and carrolites are largely hosted in the S.D.3a, S.D.2d, S.D.2a carbonaceous beds (Table 1). Towards the base of the Mines sequence, there are chalcopyrite, carrolite and minor bornite hosted in evaporitic (pseudomorph after anhydrite) dolomite and dolomitic shale beds of the upper orebody (B.O.M.Z., "Black Ore Mineralised Zone", and S.D.B., "Shales Dolomitiques de Base"/Basal Dolomitic Shale Members), and alternating millimetre- to centimetre-thick layers of silicified dolomite and shales (R.S.F., "Roches Siliceuses Feuilletées" Member), arenitic dolomite (D.Strat., "Dolomie Stratifiée" Member), and chlorite-dolomite-rich arenite (Grey R.A.T., "Roches Argilo-Talqueuses Grises" Member) of the lower orebody (see Table 1). Sulphides occur as:
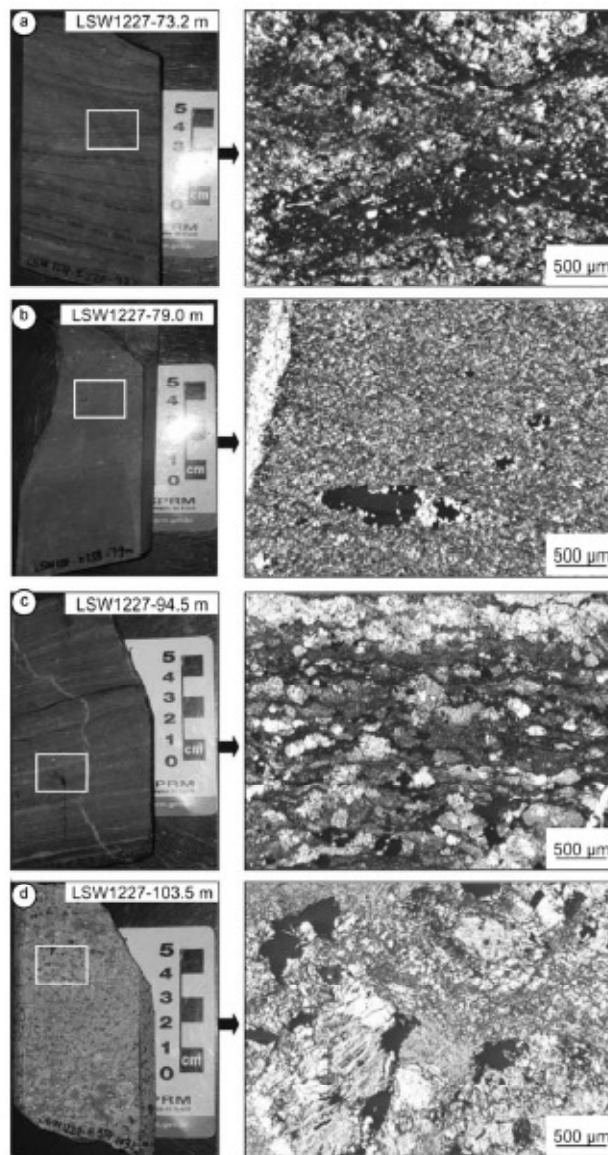
Fig. 2. Micrographs of the drillhole samples and of the corresponding polished thin sections of the major lithologies and mineralization. (a) Sample LSW1227-73.2 m—Kamibove Formation—siliciclastic dolomite containing black layers of organic matter, rich in clasts of quartz. (b) Sample LSW1227-79 m—Dolomitic Shales Formation, S.D.3b Member—arenitic dolomite free of organic matter and cross-cut by an undeformed dolomite veinlet-sulphides are disseminated and show discrete pressure shadows infilled by dolomite. (c) Sample LSW1227-94.5 m—Kamoto Dolomite Formation, R.S.F. Member—grey monogenic siltite consisting mainly of polycrystalline quartz clasts, minor sulphides and carbonates in an abundant fine-grained matrix of quartz and muscovite. (d) LSW1227-103.5 m—Kamoto Formation, Grey R.A.T. Member—the rock consists of disseminated sulphides associated with patches of coarse-grained dolomite, talc and clinochlore in a fine-grained matrix of the same composition.

(1) early disseminations and layers of chalcopyrite and carrolite, parallel to the bedding; (2) late stockwork sulphides, cross-cutting the bedding and the early sulphide generation. Sixteen samples were selected for detailed investigation.

Samples LSW1227-59.0 m and LSW1227-73.2 m (Kambove Formation) contain minor pyrite and traces of sphalerite disseminated in a siliciclastic dolomite containing fine layers of organic matter. An abundance of micron-sized clasts varies with the bedding. LSW1227-59.0 m is poor in clasts and in organic matter. LSW1227-73.2 m is richer in clasts, especially in the organic-matter rich layers (Fig. 2a). The clast fraction includes mainly angular quartz and minor rounded grains of greenish to brown tourmaline and rutile. Detrital tourmaline is always surrounded by a secondary crystallization of colourless tourmaline, and is a Fe-rich tourmaline (close to schörl end-member), whereas the secondary one is a Mg-rich tourmaline (close to the dravite end-member; Fig. 3). The matrix consists dominantly of dolomite with minor apatite

and muscovite. Both samples are affected by a schistosity, oblique to the bedding and underlined by recrystallization of some micritic dolomite, and by organic matter and muscovite.

In sample LSW1227-76.4 m (S.D.3b), chalcopyrite and carrolite form millimetre-thick bedding-parallel layers hosted in organic matter-rich siliciclastic shale. Clasts of muscovite, carbonate and greenish to brown tourmaline are also abundant.

LSW1227-79.0 m (S.D.3a) shows disseminated, frequently associated, grains of chalcopyrite and carrolite, aligned along the bedding in an organic matter-free arenitic dolomite, that immediately underlie the carbonaceous bed of the "S.D.3b" unit (Fig. 2b). The rock is deformed and cross-cut by a quite undeformed network of dolomite veinlets. The deformation is characterised locally by elongated dolomite grains and by pressure shadows associated with sulphides, indicating that sulphides were formed before deformation related to the Lufilian arc.
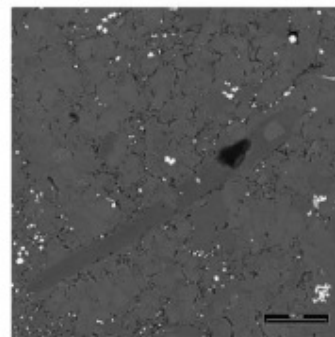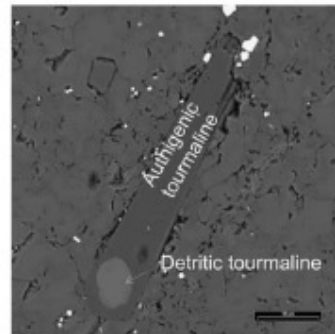
		detrital grain of tourmaline	authigenic tourmaline
K2O		0,07	0,04
SiO2		35,22	38,10
FeO		14,10	0,12
Na2O		1,69	2,81
CaO		0,17	0,36
Al2O3		34,58	33,13
MnO		0,15	0,00
MgO		0,59	10,24
TiO2		0,18	0,05
Cr2O3		0,13	0,05
BaO		0,00	0,20
NiO		0,05	0,00
Cl		0,01	0,00
F		0,67	0,00
H2O		1,52	1,59
		89,12	86,67
Structural formulae on the base of 29 O			
K		0,018	0,010
Si		6,963	7,200
Fe		2,331	0,018
F		0,416	0,000
Na		0,648	1,028
Ca		0,037	0,073
Al		8,055	7,378
Mn		0,025	0,000
Mg		0,174	2,885
Ti		0,026	0,007
Cr		0,021	0,007
Cl		0,002	0,000
Ba		0,000	0,015
Ni		0,008	0,000

Fig. 3. Sample LSW1227-73.2 m—Kambove Formation—back-scattered electron image of a Fe-rich tourmaline detrital grain rounded by authigenic Mg-rich tourmaline growth. Chemical analyses of both types of tourmaline are given.

In sample LSW1227-84.0 m (S.D.2d), the sedimentary host rock consists of black organic matter-rich shale with rare and thin chalcopyrite layers aligned along the bedding and crosscut by carrolite–carbonates veinlets. Sample LSW1227-87.5 m is a dolarenite bed poor in organic matter which is part of the carbonaceous "S.D.2a" Member, and showing disseminated chalcopyrite. Sample LSW1227-92.0 m is a finely bedded rock with alternation of silicified dolomite and dolomitic shale interbedded in the R.S.C. Member. Dolomitic shale lithology is rich in organic matter and contains many bedding-parallel carrolite–carbonate layers. LSW1227-93.5 m (R.S.F.) is a finely bedded organic matter-rich siliciclastic shale including millimetre- to centimetre-thick quartz layers with chalcopyrite and carrolite disseminated grains. Muscovite flakes and clasts of greenish to brownish tourmaline occur in the black shale layers.

LSW1227-94.5 m (R.S.F.) is a grey monogenic siltite including rare quartz-dolomite layers. It consists mainly of polycrystalline quartz clasts with minor sulphides—chalcopyrite and carrolite—and carbonates (Fig. 2c). Magnesite is the main carbonate associated with sulphides. Some textures point to mineral replacement. A clast containing Ti-rich biotite (2.3 wt% TiO_2) indicates a detrital component from medium-grade metamorphic rocks. The matrix is abundant and mainly made of fine-grained muscovite and microcrystalline quartz, with disseminated dolomite. The bedding is cross-cut by medium-grained quartz + magnesite ± dolomite–chalcopyrite–carrolite veinlets. Sample LSW1227-100 m ("D.Strat.") includes chalcopyrite–carrolite–dolomite ± magnesite–quartz–apatite stockwork hosted in an organic matter-free stratified dolarenite.

Sample LSW1227-101 m (Grey R.A.T.) is a siltite formed by abundant angular quartz clasts, rare clasts of greenish tourmaline, embedded in a fine-grained clinochlore matrix. Dolomite ± quartz pseudomorphs after gypsum and anhydrite are abundant. Chalcopyrite occurs as small patches and veinlets, always associated with clinochlore and quartz.

Sample LSW1227-103.5 m (Grey R.A.T.) consists of an entirely recrystallised rock, marked by: (1) patches of chalcopyrite associated with coarse-grained dolomite, talc and clinochlore, (2) a fine-grained matrix of the same composition (Fig. 2d).

4. Isotope analyses

4.1. Analytical techniques

Chalcopyrite and carrolite were separated by handpicking under a binocular microscope after a slight crushing of the sample. Analyses of sulphur isotopes on sulphides were performed at the BRGM Laboratory. About 10 mg of sulphide were reduced to a very fine powder and analyzed for sulphur isotope composition by combustion under an oxygen pressure, according to the method of Thode et al. (1961). The SO_2 gas obtained was purified using successively a dry ice trap and a variable-temperature trap successively regulated at −145 °C, −150 °C and −90 °C, to eliminate possible traces of water and carbonic gas, respectively. Their sulphur isotopic composition was determined using a Delta S Finnigan-Mat gas source mass spectrometer. Results are reported in δ notation relative to Canyon Diablo Troilite (CDT) international standard for sulphur

Table 2
Sulphur isotopic compositions of sulphides from the Luiswishi Cu–Co ore deposit

Depth	Formation/member	Ore/type/OM	$\delta^{34}S_{Cpy}$ (CDT), ‰	$\delta^{34}S_{Car}$ (CDT), ‰
Drillhole 1227				
59.0 m	Kambove Formation	Py		
73.2 m	Kambove Formation	Py		
76.4 m	S.D.3b Member	Cpy + Car/type 1/OM	+5.8	−8.4
79.0 m	S.D.3a Member	Cpy + Car/type 1	−12.3	−10.2
84.0 m	S.D.2d Member	Cpy/types 1–2/OM	−11.6	−13.1
87.5 m	S.D.2a Member	Cpy/type 1	−6.9	
92.0 m	Interc. R.S.C. Member	Car/type 1/OM		−3.2
93.5 m	R.S.F. Member	Cpy	0.0	−3.0
94.5 m	R.S.F. Member	Cpy + Car ± Bor/type 1	+2.5	+8.4
100.0 m	D.Strat. Member	Cpy + Car/types 1–2	+10.9	+13.6
101.0 m	Grey R.A.T. Member	Cpy + Car ± Bor/types 1–2		
103.5 m	Grey R.A.T. Member	Cpy ± Bor/type 2	+17.5	
Drillhole 1215				
63.0 m	S.D.2d Member	Cpy/type 1/OM	−14.2	
79.5 m	B.O.M.Z. Member	Cpy/type 1	−3.1	
Surface-level 1300–1305				
1A	Grey R.A.T. Member	Cpy + Car ± Bor/type 2		+10.6
2A	Grey R.A.T. Member	Cpy + Car ± Bor/type 2	+11.3	+11.9

Precisions concerning the Formation or the Member to which the sample belongs, the nature of separated sulphides, the type of ore and the presence of organic matter are also given. Type 1 corresponds to early dissemination and bedding-parallel layers of chalcopyrite (Cpy) and carrolite (Car), and type 2 to late stockwork sulphides cross-cutting the bedding and the early sulphide generation. Bornite (Bor) is accessory. OM indicates the significant presence of organic matter.
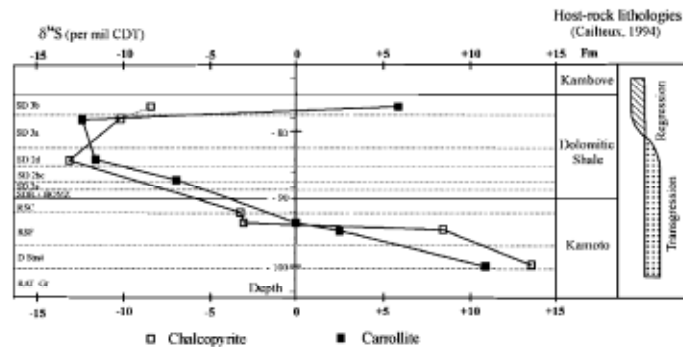
Fig. 4. Sulphur isotopic composition of chalcopyrite (black squares) and carrolite (white squares) related to the Mines Subgroup lithostratigraphy, according to Cailteux (1994) and Cailteux et al. (2003).

isotopes. During the investigation period, three standards were analyzed for sulphur isotopes in the laboratory. The $\delta^{34}S$ of the international standard NBS127 was $+20.2 \pm 0.4\%_0$ (reference value: $+20.3 \pm 0.4\%_0$, IAEA, 1995) and the $\delta^{34}S$ of the international references IAEA-S2 and IAEA-S3 were, respectively, $+21.5\%_0$ and $-32.0\%_0$ (respectively, reference values: $\sim+22\%_0$ and $\sim+32\%_0$, Coplen and Krouse, 1998).

4.2. Results

Sulphides (chalcopyrite and carrolite, disseminated in bedding-parallel layers and in veins) were analyzed for sulphur isotopes from the sixteen samples described above.

The results show a large range of $\delta^{34}S$ values, between $-14.2\%_0$ and $+17.5\%_0$ for chalcopyrite and $-10.2\%_0$ to $+13.6\%_0$ for carrolite (Table 2). The most negative $\delta^{34}S$ values occur in samples from the Dolomitic Shales Formation, and the most positive ones from the Kamoto Formation. Distribution of these values is strongly controlled by lithostratigraphy, decreasing from "D.Strat." to "S.D.2d"– "S.D.3a" Members and increasing from "S.D.2d"– "S.D.3a" to "S.D.3b" Members (Fig. 4).

$\delta^{34}S$ values of stratiform sulphides (disseminated and bedding-parallel layers) range between $-14.2\%_0$ and $+17.5\%_0$ for chalcopyrite and between $-13.1\%_0$ and $-3.0\%_0$ for carrolite, whereas those from veins and stock-works range between $+2.5\%_0$ and $+11.3\%_0$ for chalcopyrite and between $-13.1\%_0$ and $+13.6\%_0$ for carrolite. In sample LSW1227-84.0 m, disseminated chalcopyrite in bedding parallel layers shows the same $\delta^{34}S$ variation trend as carrolite in veinlets. The fractionation between coexisting chalcopyrite and carrolite of the same type is heterogeneous, ranging from $-5.9\%_0$ to $+14.2\%_0$, whatever the type of sulphide (early stratiform or late stockwork). In organic matter (OM)-rich samples, $\delta^{34}S$ of chalcopyrite is systematically higher than $\delta^{34}S$ of carrolite.

5. Discussion

Since the discovery of the Copperbelt in the 1900s, several genetic models have been proposed to constrain the sources of metals and sulphide, and the ore deposition processes (see Cailteux et al., this issue, and references therein). The first two major hypotheses, epigenetic and syngenetic, were both unsatisfactory. A diagenetic model (e.g., Bartholomé et al., 1972; Bartholomé, 1974) based on the existence of two generations of sulphides in the orebodies, appeared to be attractive, defining: (1) an earliest copper–(cobalt)–sulphide generation which grew during the deposition and the early-diagenetic stage of the host-sediments; (2) a second copper–(cobalt)–sulphide generation formed during a large scale chemical reaction between the host-sediment interstitial water and a metal-bearing brine. However, this model does not address the origin of solutions, primary source of metals, and exact timing of mineralisation (?early, ?late diagenesis). These unknowns led to the syn-diagenetic and diagenetic-hydrothermal alternative hypotheses, linking the mineralising fluids respectively to: (1) influx of most of the metals to the Katangan sedimentary basin by erosion of the pre-Neoproterozoic basement terrains, and mixing of oxidized mineralising, enriched brines from a hypersaline lagoon setting with interstitial reducing water rich in organic compounds (Renfro, 1974; Cailteux, 1986; Sweeney and Binda, 1989; Sweeney et al., 1991; Cailteux et al., this issue); (2) late diagenetic hydrothermal fluids originating from mafic igneous rocks or rift related processes (Annels, 1974, 1979, 1989; Annels and Simmonds, 1984; Lefebvre, 1989; Unrug, 1988).

By comparison, the Copperbelt ore deposits are distinct from other sediment-hosted stratiform copper deposits in many aspects, such as their host lithologies, metal ratios and the timing of metal influx relative to sedimentation and diagenesis. However they show common features of genetic importance. They are considered to be syndiagenetic

deposits such as the Kupferschiefer-type (Kirkham, 1996) and red-bed-type (Davidson, 1965; Brown and Chartrand, 1986; Brown, 1992; Haynes, 1986; Ohmoto, 1986; Rose, 1989; Walker, 1989), whose main source of metals was from the leaching or dewatering of formations lying stratigraphically beneath the ore deposits. Ore occurs in chemically anoxic, sulphur-rich grey beds lying immediately on oxic continental red beds, just above a fossil redoxcline. The anoxic environment results from the presence of carbonaceous matter, and abundant sulphides result from the biogenic reduction of primary and early diagenetic sulphates at low temperature (<50 °C). Origin of sulphate is still debated. The major source of sulphate remains marine or saline-lacustrine (Ohmoto, 1986; Ohmoto et al., 1990); however a significant portion of sulphur could have been introduced into the oxidized ore solution at Kamoto (Hoy and Ohmoto, 1989).

Sulphur isotopes are important data in determining the source of sulphur and conditions of ore deposition, and therefore contribute to the debate. The large sulphide $\delta^{34}S$ variations at Luiswishi (between −15‰ and +17‰) are consistent with isotopic data obtained in other stratiform copper ore deposits of the Copperbelt (Dechow and Jensen, 1965; Schwarcz and Burnie, 1973; Ohmoto, 1986; Okitaudji-Lokoho, 1989; Sweeney et al., 1986, 1991) but also of the world (e.g., Kupferschiefer in Germany, Bechtel et al., 2001; White Pine in Canada, Burnie et al., 1972).

The large range in $\delta^{34}S$ values of chalcopyrite and carrolite at Luiswishi are similar and reflect variations as a function of the lithological succession, as was previously shown at Konkola (Sweeney et al., 1986, 1991). Progressive negative and positive $\delta^{34}S$ values of sulphides may be correlated with lithological transgressive–regressive evolution of the ore-hosting sedimentary rocks (Cailteux, 1994) (Fig. 4). Moreover, the sulphur isotopic fractionation between chalcopyrite and carrolite systematically changes with the presence of organic matter. That indicates a strong stratigraphical control of the sulphide $\delta^{34}S$ and provides evidence of early processes of sulphide formation by bacterial reduction of sulphates, partly favoured by carbonaceous matter in an anoxic environment.

Negative and positive $\delta^{34}S$ values can be interpreted, respectively, in open (transgression) and relatively closed (regression) systems for SO_4^{2-} (Ohmoto and Rye, 1979). High positive sulphur isotopic signatures of sulphides, near $\delta^{34}S$ of marine sulphates, occurs at the bases of the orebodies at Luiswishi, indicating ore deposition in a closed basin cut off from seawater, as was also demonstrated at Konkola in Zambia (Sweeney et al., 1986). At Kamoto, chalcocite and chalcocite + bornite in the Grey R.A.T. Member show negative $\delta^{34}S$ (Dechow and Jensen, 1965); however a tendency to an increase of the $\delta^{34}S$ in this member relative to the D.Strat. member is observed. The comparable isotope profiles along the lithologic succession at Luiswishi in Congo and at Konkola in Zambia show, however, some differences, with a continuous transgressive regime in the orebody-hangingwall sequence at Luiswishi in Congo,

whereas a regressive episode occurs at the top of the Ore Shale at Konkola (Sweeney et al., 1986). Elsewhere the lack of data and of comparative information concerning the sampling do not allow inferences about depositional conditions of the orebodies at the scale of the Copperbelt.

The sulphide isotopic data of Luiswishi, similarly to most of the stratiform copper ore deposits of the Copperbelt (Dechow and Jensen, 1965), show a broad distribution centered about zero and ranging up to $\delta^{34}S$ of seawater. These can be compared with the data of the White Pine ore deposit (Burnie et al., 1972) and suggest dominant shallow marine or saline-lacustrine sources for the original sulphate. A small portion of sulphur may have been introduced in the ore solution as proposed by Hoy and Ohmoto at Kamoto (1989); $\delta^{34}S$ of anhydrite from nodules in the Mine succession (+16‰ to +23‰, Dechow and Jensen, 1965; Okitaudji-Lokoho, 1989; Sweeney et al., 1986) are quite close to sulphate $\delta^{34}S$ of Neoproterozoic seawater (Claypool et al., 1980; Krouse, 1980; Hurtgen et al., 2002); this strongly suggests that this external sulphate contribution was slight relative to the inferred marine sulphate source.

The rare $\delta^{34}S$ data obtained on both early stratiform and late stockwork sulphides in the same samples of Luiswishi are comparable. That strongly suggests a similar origin of the sulphur for both generations of sulphides, and a local-scale reworking of the early stratiform sulphides during the tectono-metamorphic Lufilian orogeny. This reworking was not strong enough to re-equilibrate the $^{34}S/^{32}S$ ratios under metamorphic conditions. Consequently, sulphur isotopic data do not provide evidence for introduction of a new sulphur source in compacted sediments of the Copperbelt during the Lufilian orogeny.

6. Conclusions

Sulphur isotope compositions were analyzed on sulphides (chalcopyrite and carrolite, where possible) of different lithostratigraphic units of the Mine Series, hosting the Cu–Co orebodies in the Luiswishi ore deposit. The $\delta^{34}S$ values range from −14.4‰ in the S.d.2d member up to +17‰ at the bottom of the Kamoto Formation. The large distribution of sulphide $\delta^{34}S$ values centered on zero suggests a strong stratigraphic control of the sulphur isotope signature, supporting bacterial reduction of marine sulphates during sedimentation and diagenesis in a shallow marine or lacustrine environment. The systematic reverse of the chalcopyrite–carrolite sulphur isotopic fractionation in the presence of organic matter indicates that organic matter strongly controlled both bacterial sulphate reduction and ore deposition. Sulphides of the lower orebody at Luiswishi were probably deposited during a period of regression in a basin closed to seawater. The variations of $\delta^{34}S$ values along the lithologic succession are in perfect agreement with the lithological transgressive–regressive evolution of the ore-hosting sedimentary rocks (Cailteux, 1994). Those conditions are quite similar to those described

at Konkola (Zambian-type Cu–Co ore deposit) by Sweeney et al. (1986). The introduction of an external sulphur source during diagenesis, as proposed by Hoy and Ohmoto (1989), remains subject to debate. Relics of sulphates in the Mines succession hosting orebodies are quite close to seawater sulphates and no petrological feature of the samples provides evidence of any significant hydrothermal contribution.

The quite similar $\delta^{34}S$ values of stratiform sulphides and late stockwork sulphides related to the Lufilian orogeny suggest an in situ recrystallization or a slight remobilization of stockwork sulphides without attainment of isotopic equilibrium between the different sulphide phases (chalcopyrite and carrolite). It also provides no evidence for external input of sulphur in compacted sediments during the Lufilian tectono-metamorphic event.

Acknowledgements

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